

Electron beam damage in high temperature polymers

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Electron microscopic studies of polymers are limited due to beam damage. Two concerns are the damage mechanism in a particular material, and the maximum dose for a material before damage effects are observed. From the knowledge of the dose required for damage to the polymer structure, optimum parameters for electron microscopy imaging can be determined. In the present study, electron beam damage of polymers has been quantified by monitoring changes in the diffraction intensity as a function of electron dose. The beam damage characteristics of the following polymers were studied: poly(*p*-phenylene benzobisthiazole) (PBZT); poly(*p*-phenylene benzobisoxazole) (PBO); poly(benzoxazole) (ABPBO); poly(benzimidazole) (ABPBI); poly(*p*-phenylene terephthalamide) (PPTA); and poly(aryl ether ether ketone) (PEEK). Previously published literature results on polyethylene (PE), polyoxymethylene (POM), nylon-6, poly(ethylene oxide) (PEO), PBZT, PPTA, PPX, iPS, poly(butylene terephthalate) (PBT), and poly(phenylene sulphide) (PPS) were reviewed. This study demonstrates the strong dependence of the electron beam resistivity of a polymer on its thermal stability/melt temperature.

(Keywords: electron beam damage; high temperature polymers)

INTRODUCTION

Careful consideration of the radiation damage characteristics of polymers is important for certain applications. Electronic applications and use of polymers in space (damage due to cosmic rays in space) are two such applications where radiation damage resistance is required. Polymer damage may also occur during characterization by means of radiation such as X-rays, neutrons and electrons. Among these, the electron beam damage problem has been the most severe because the typical dose rate for high resolution transmission electron microscopy is of the order of 10^{11} rad/s. The focus of this paper is on polymer structure damage due to electrons in transmission electron microscopy. This study was intended to examine the conditions for optimum imaging. What can be learned from this type of damage study in the transmission electron microscope relevant to the damage in actual applications, such as in electronics or in space, remains to be examined.

Radiation can affect a number of properties which can be used for quantitative study of the damage. Some of these are mass loss, loss of order or crystallinity, change in tensile properties (stiffness and strength), change in electrical conductivity, change in the coefficient of thermal expansion, and variation in transport properties. In the present study, loss of order or crystallinity has been used as the criterion for quantifying the damage. This has been done by monitoring the electron diffraction intensity of one or more reflections as a function of electron dose. However, it should be noted that a number of other polymer characteristics continue to change, even after crystallinity has disappeared.

Studies on various aspects of electron beam damage of polymers¹⁻²⁴ and other organic materials²⁵⁻³³ have been undertaken. Diffraction intensity has been shown to decrease exponentially^{5,7} with increasing electron dose. The intensity, $I(D)$, of a particular reflection at a dose, D , has been given by the following equation.

$$I(D) = I_0 e^{-D/D^*} + I_\infty$$

where I_0 is the intensity of that reflection for zero dose and D^* is defined as the characteristic dose at which the intensity is reduced by a factor of $1/e$. I_∞ is the intensity at infinite dose, or at a dose at which no further change in intensity is observed. In practice, $I(D)$ is usually measured from microdensitometer traces of the electron diffraction negatives, and background intensity is subtracted from each diffraction peak. This therefore assumes that $I(D)$ falls to this background level (I_∞) at high dose. Changes occurring due to beam damage do not always follow a single exponential function, and are slower at higher exposures¹⁹.

The first detailed work on the effect of an electron beam on polymers was reported by Kobayashi and Sakaoku¹ on a number of polymers including PE, POM, PEO, and Nylon-6. It was observed that the resistance of the crystals to decay in the electron beam seemed to be related to their melting points. However some complications were observed, for example, a single crystal of poly(vinyl alcohol) showed less resistance in the electron beam than a nylon crystal. Both materials have nearly the same melting points and both have hydrogen bonding between their molecular chains. Thermal decomposition of the polymer due to heat generation because of electron bombardment is not likely. Under typical TEM imaging conditions, temperature rise of less than 30°C is predicted³⁴.

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From the study of the electron beam effect on the fracture of a number of polymers (Kevlar-49 fibre, polyisoprene, butyl rubber, polybutadiene, and high density polyethylene) it was concluded that the electron beam induced fracture is due to bond breaking and that it was not a thermal phenomenon^{3,4}.

Encapsulation³² of the specimen by carbon coating is reported to reduce the beam damage at room temperature by a factor of 3 to 12. Beam damage characteristics of polymethyl methacrylate (PMMA), poly(oxymethylene) (POM), poly(vinyl chloride) (PVC), and the blends of (PMMA/POM) and (PVC/POM) were studied using mass loss characteristics¹⁹.

Radiation damage characteristics of UltemTM and KaptonTM were studied using electron radiation doses of up to 6 giga rad²². This radiation is equivalent to the radiation received by a material in 30 years in geosynchronous orbit. The materials were irradiated at a dose rate of 1 giga rad/h at a temperature of 35 to 38°C. At the above dose conditions, significant mechanical property changes were observed in UltemTM while mechanical property changes in KaptonTM were not very significant. Greater changes in UltemTM were attributed to the presence of methyl groups (the aliphatic hydrogen)²², because the hydrogens from gem-dimethyl groups in UltemTM were attracted by phenyl radicals. In KaptonTM no aliphatic hydrogen was available and therefore it is presumed that radical-radical recombination took place.

A full review of electron radiation effects in polymers is given by Sawyer and Grubb³⁴ and Grubb³⁵.

EXPERIMENTAL

Chemical repeat units of various materials investigated in the current study are given in Figure 1. Fibres of PBZT, PBO, ABPBO, ABPBI, and PPTA were detached using parlodion in order to prepare thin sections for electron diffraction. Thin specimens of PEEK film were prepared by ultramicrotomy.

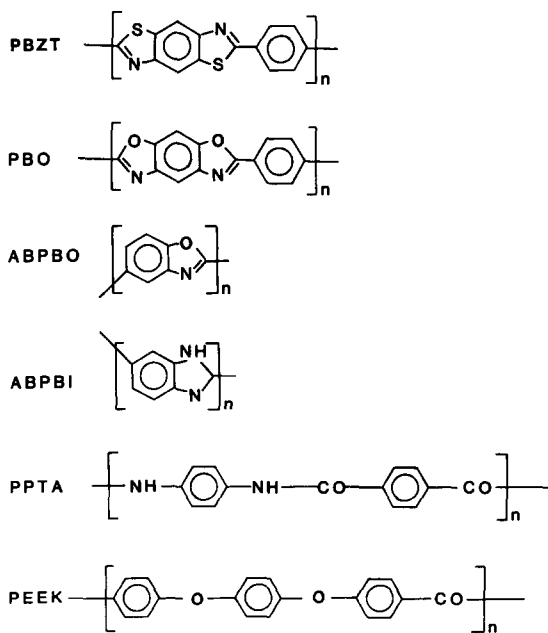


Figure 1 Chemical repeat units of various polymers investigated in this study

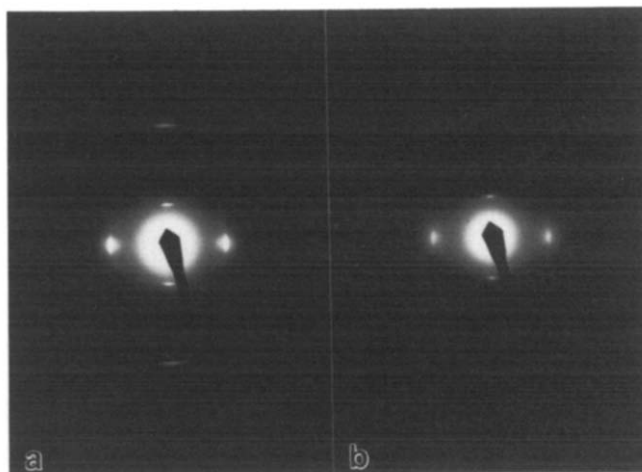


Figure 2 Electron diffraction patterns of Kevlar-29. (a) Initial and (b) at $25 \times 10^{-2} \text{ C/cm}^2$ dose

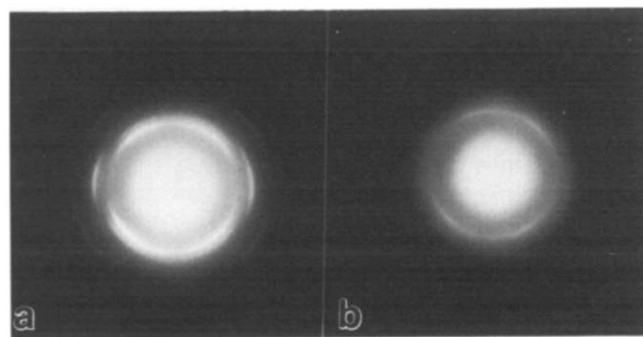


Figure 3 Electron diffraction patterns of PEEK, (a) initial and (b) at $21 \times 10^{-2} \text{ C/cm}^2$ dose

Beam current was determined using a Faraday cup, and the irradiated specimen area was separately monitored for a particular condenser aperture at given condenser lens currents. For PBZT, PBO, ABPBO, PPTA, and ABPBI electron diffraction patterns were photographed at successive intervals. Changes in the intensities of individual reflections were measured from microdensitometry and background intensity was subtracted from each peak. For PEEK, intensity variations were measured on the microscope screen using a Keithly electrometer while the individual reflections were separated using an objective aperture.

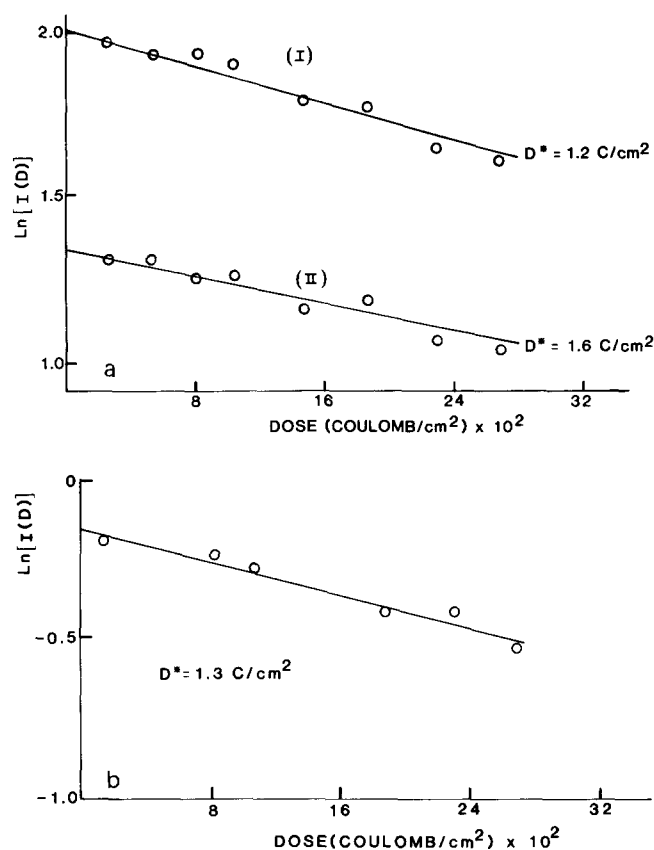
The study was done at room temperature on a Jeol 100 CX electron microscope operated at 100 kV. The specimens were irradiated at an approximate dose rate of $2.5 \times 10^{-4} \text{ A/cm}^2$. The temperature change during irradiation was not monitored. However, the low dose rate used is unlikely to significantly increase the specimen temperature.

RESULTS AND DISCUSSION

Electron diffraction patterns from undamaged and damaged PPTA and PEEK are given in Figures 2 and 3, respectively. In both cases significant intensity reduction of reflections is evident. Similar intensity reductions are observed in other polymers reported in this paper. This intensity variation for these polymers with increasing electron dose has been used to determine the value of

Table 1 *d*-Spacings (nm) of various polymers. *d*-Spacings used to determine D^* values are underlined

	PBZT	PBO	ABPBO	ABPBI	Kevlar™	PEEK
Equatorial	<u>0.583</u>	<u>0.550</u>	0.608	0.72	<u>0.433</u>	<u>0.469</u>
	<u>0.351</u>	<u>0.348</u>	<u>0.338</u>	<u>0.35</u>	(110) <u>0.388</u>	(110) <u>0.388</u>
	0.313	0.326			(200) <u>0.215</u>	(200)
Meridional	<u>1.25</u>	1.20	0.58	0.58	0.64	
	0.42	0.398	0.29		(002) 0.322	
	0.31	0.300			(004) <u>0.215</u>	(006)


Figure 4 (a) Variation of intensity for equatorial reflections of PBZT as a function of electron dose; curve I, 0.583 nm peak; curve II, 0.351 nm peak. (b) Variation of intensity for the first layer line of PBZT as a function of electron dose

the critical dose (D^*). The *d*-spacings of the strong intensity reflections for these polymers are listed in *Table 1*. The *d*-spacings which were used to determine the D^* values for these polymers have been underlined in *Table 1*. The intensity variation of the two equatorial reflections (100) and (010) (0.583 nm and 0.351 nm) and the first layer line (1.25 nm) of PBZT are plotted in *Figure 4*. In this figure, $I(D)$ is actually $I(D) - I_\infty$ from the equation in the introduction section. The D^* values calculated from these intensity variations are 1.2, 1.6, and 1.3 C/cm^2 , respectively. Similarly D^* values were obtained for PBO, ABPBO, ABPBI, PPTA (Kevlar™) fibre, and PEEK film from the corresponding reflections underlined in *Table 1*.

The D^* values thus determined for the above polymers and for a number of other polymers obtained from the literature are listed in *Table 2*. Melt temperatures or the

onset of degradation temperatures of those polymers which degrade before any melting is observed are also listed in *Table 2*. The present work was done at 100 kV, and the data for other polymers is also available from the literature at 100 kV or 120 kV. From the work of Grubb and Groves⁷ on polyethylene, polyoxymethylene, and poly-4-methylpentene, it is noted that at 120 kV the specimen is able to withstand 10–20% higher dose. By definition, the value of D^* should be less than the value of total end point dose (TEPD). Using these considerations the D^* values for all the polymers in *Table 2* can be estimated at 100 kV. These D^* values are plotted as a function of melt or degradation temperature in *Figure 5*, which shows good correlation with few exceptions. Reported stability of PPS is significantly higher than would have been predicted from this correlation; observed stability of PBO is somewhat lower. For PPS we had the value of total end point dose (TEPD) and if changes in the later stages of degradation were lower then the D^* value could be significantly different.

To our knowledge this is the first time that such a correlation has been shown over this wide temperature range (300–1000 K) for polymers, though it has often been assumed and has previously been reported in a limited temperature range¹. The correlation in *Figure 5* is not to be mistaken with any temperature rise in the specimen. During the exposure to the electron beam, the specimen temperature was not monitored. However, under the exposure conditions (thin specimens < 100 nm, 100 kV, low dose rate of $2.5 \times 10^{-4} \text{ A/cm}^2$) significant temperature rise is not expected. The specimen damage in the electron beam can be attributed to selective bond breakage and their subsequent inability to recombine. The bond breakage leads to radical formation which contributes to crosslinking in certain polymers. A more

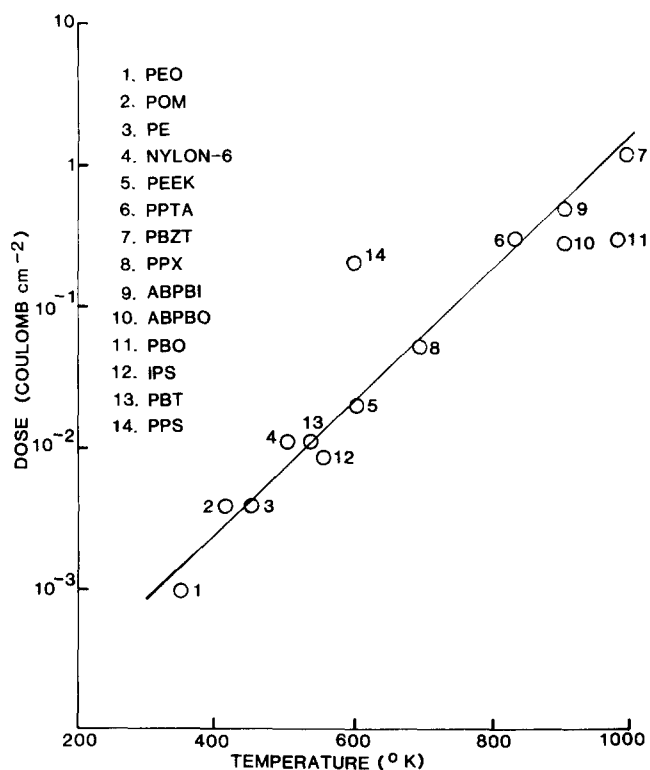

Figure 5 Correlation between critical electron dose (D^*) and specimen melt temperature (or onset of degradation temperature) for those polymers which degrade before any melting is observed)

Table 2

Polymer	D^* (C/cm ²) ^a	Melt/degradation temperature (°C)	Ref.
PEO	0.00046 (120 kV, TEPD ^b) 0.0012–0.0021 (200 kV)	66–72	1, 2
PE	0.0031 (120 kV, TEPD) 0.0043 (100 kV) 0.012 (125 kV) 0.014–0.02 (500 kV) 0.024 (1000 kV)	137	1, 2, 7
POM	0.01 (100 kV)	180	1, 7
Nylon-6	0.02 (100 kV)	215–225	1
iPS	0.018 (120 kV, TEPD)	240	2
Poly(butylene terephthalate)	0.015	250–260	37
PEEK film	0.03–0.06 (100 kV)	335	This work
PPS	0.31 (TEPD)	315	38, 39
PPX(α)	0.048 (120 kV), 0.5 (500 kV)	375–400	2
PPX(β)	0.062 (120 kV), 0.5 (500 kV)	412–420	2
PPTA fibre	0.4–0.5 (100 kV) (equatorial and meridional)	550 in He (505 in air)	This work
ABPBI film	0.65 (100 kV)	640 in He (535 in air)	This work
ABPBO fibre	0.13 (equatorial) 0.46 (meridional) (100 kV)	640 in He (625 in air)	This work
PBO fibre	0.16 (equatorial)	685 in He (635 in air)	This work
PBZT fibre	1.2–1.6 (equatorial and meridional)	710 in He (580 in air)	This work and ref. 5

^a 1 C/cm² = 625 electrons/Å²

^b TEPD = total end point dose

thermally stable polymer requires more energy for the damage. This argument is intuitive and is not unexpected. However, other factors such as morphology and history of the material (such as heat treatment) will also have some effect on the damage characteristics. Chemical composition (types of chemical bonds present³⁴) of the material, of course, has some influence as evidenced from the difference in poly(vinyl alcohol) and nylon, where both materials have nearly the same melting points and both have hydrogen bonding, but single crystals of poly(vinyl alcohol) were reported to have less resistance in the electron beam than nylon single crystals¹. Reported differences²² in the mechanical properties of UltemTM and KaptonTM on irradiation also suggested differences other than those due to their thermal properties.

Specimen stability has been shown to increase with a decrease in the observation temperature at which the specimen has been maintained in the microscope⁷. This can be attributed to the greater possibility of recombination of chemical bonds at lower temperature because of reduced molecular mobility. The probability of recombination of a broken bond will be higher if the other bonds in its vicinity are intact. At a lower dose rate there would be fewer broken bonds at any given time, therefore the probability of recombination of bonds will also be higher at the lower dose rates, though the effect may be smaller. If the dose rate effect is indeed significant then it will have to be taken into account for predicting the material properties in, for example, a geosynchronous orbit. Results by Krause *et al.*¹¹ indicate that dose rate effects may be significant. However, some of the earlier work²⁸ indicated negligible dose rate effects. Recent work by Fryer³³ seems to suggest less damage at higher dose rate. Further work will be required to confirm any dose rate effects.

Table 3 Unit cell parameters of PEEK as a function of electron irradiation dose

Electron dose C/cm ²	a (nm)	b (nm)	c (nm)
4.2×10^{-2}	7.74	5.91	9.87
8.4	7.80	5.92	10.11
12.6	7.84	5.95	10.31
21.0	7.92	6.01	
% change for above dose	2.3%	1.7%	4.5%

 Table 4 Change in d -spacings for the given electron dose

Polymer	Reflection	% change in d -spacing	Electron dose C/cm ²
PPTA	(006) (110)	decreases 1.4% increases 1.4%	25×10^{-2}
PBZT	(100) (010)	decreases 1.7% increases 4%	25×10^{-2}
PBO	(100) (010)	decreases 2.5% increases 12%	12×10^{-2}
ABPBO	No significant change observed within the limits of experimental error		12×10^{-2}

Unit cell dimension changes in PEEK as a function of electron dose are listed in Table 3. Unit cell dimensions increased in all three directions, and the maximum change was observed along the c -axis. Observed changes in the d -spacings of the other polymers are listed in Table 4. For PPTA the spacing along the chain decreased, and the spacing perpendicular to the chain increased. Hydrogen from the N–H bond is probably the first atom to be removed from the structure, therefore eliminating or reducing the number of hydrogen bonds. This may result in increased equatorial d -spacings.

The meridional d -spacings of the PBZT and PBO and equatorial and meridional spacings of ABPBO and ABPBI either could not be monitored sufficiently accurately or no significant changes were observed in them. The 0.583 nm PBZT and 0.550 nm PBO spacings decreased while the 0.351 nm PBZT and 0.348 PBO spacings increased, with larger changes being observed for PBO than for PBZT. The PBO molecular structure is *cis* while PBZT is in a *trans* configuration. Another difference between the two is that sulphur atoms in PBZT have been replaced by oxygen atoms. The larger d -spacing change in PBO compared to PBZT must arise due to the above two differences in their structures. These differences will also be responsible for the slightly lower D^* value for PBO than for PBZT even though their thermal stability is not much different. These observations indicate that the C–O and C–S bonds in PBO and PBZT, respectively, are the first ones to break during electron exposure. WAXS studies on PBZT fibre as a function of temperature resulted in increased d -spacings with temperature for both (100) and (010) reflections³⁶. This indicates that the d -spacing change observed with exposure to electron beam is of a different nature than the d -spacing change observed due to thermal expansion/contraction. This observation further confirms that the specimen temperature did not rise significantly. Similar conclusions were drawn by Kobayashi and Sakaoku¹ indicating that the changes in the crystal lattice in an irradiated specimen are quite different from that due to thermal expansion.

CONCLUSIONS

This study demonstrates that the stability of a polymer structure in the electron beam is strongly dependent on its thermal stability/melt temperature. Among the polymers reported, PBZT is the most stable polymer in the electron beam, with the other aromatic heterocyclic polymers and PPTA being nearly as stable. The d -spacing changes as a function of electron dose have been reported, and it has been shown that the changes are of a different nature than observed by heating the specimen. It has been argued that the beam damage was not a result of temperature increase, but further work is required to elucidate the damage mechanism in different polymers and to explain why it correlates so well with melt/ degradation temperature.

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